

STAT

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Electrolysis of Nickel

by

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Zhurnal Prikladnoy Khimi [Journal of Applied Chemistry],
Vol 24, No 6, pp 604-609, Russian (article) Mo per, Jun 51

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FORMATION OF HYDRATES UNDER CONDITIONS OF NICKEL ELECTROLYSIS

[Report No. III of a series of works in this field]

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In the preceding contributions [1,2] we examined the conditions under which colloid hydrates of nickel, copper and iron begin to form in the electrolyte used for the electrolytic refining of nickel.

In this article we bring the results of experiments on the influence of the anion of salts and of the nature of buffer admixtures on the value of pH at the moment when the nickel hydrates begin to form. We also discuss the entire experimental material.

The experimental methodology does not differ from that described in the first report. The experimental data is given in Figures 1, 2 and 3, and in Tables 1 and 2. The beginning of hydrate formation is indicated with arrows on the titration curves. The data for the sulphate solutions is taken from the first report.

FIGURE 1

Potentiometric Titration Curves of a pure NiCl_2 Solution and of one with Buffer Admixtures. $t=50$ degrees centigrade. (A) Electromotive force (in mV); (B) Amount of NaOH (in milligrams). Solution Composition: (1) 38 g/l Ni; (2) 38 g/l Ni+0.16 mol/l H_3BO_3 ; (3) 38 g/l Ni+0.16 mol/l $(\text{NH}_4)_2\text{SO}_4$; (4) 38 g/l Ni+0.16 mol/l NH_4Cl .

In the first line of Table 1 we compare the values of pH at the initial moment of hydrate formation from pure solutions of nickel sulphate, chloride and nitrate. We see from this data that the value of pH in the hydrate formation for nitrate and chloride salts practically coincide, while the sulphate salt forms colloid hydrates in a somewhat more alkaline medium. This difference, apparently, is caused by the lower activity of nickel ions in the sulphate solution. The difference between the values of pH at the initial moment of formation of nickel hydrates in sulphate and chloride salt solutions is equal to 0.4. This coincides qualitatively with the figures cited in the first report [1].

From Table 1 we see that an admixture of boric acid to the pure salt solutions lowers the value of pH by 1.0 at the initial moment of the formation of nickel sulphate hydrates, and by 1.5 for nickel chloride and nitrate. Ammonium sulphate lowers the value of pH in the sulphate medium almost twice as much as boric acid, while in nitrate and chloride mediums the action of both the buffer admixture is the same.

Solutions of $\text{NiNO}_3 \cdot \text{NH}_4\text{Cl}$ and $\text{NiNO}_3 \cdot \text{NH}_4\text{NO}_3$ are noteworthy. For these, neither the inflexion point on the potentiometric curves corresponding to the appearance of the solid phase, nor the appearance of diffused luminescence, could be found.

FIGURE 2

Potentiometric Titration Curves of a Pure NiNO_3 Solution and of one with Buffer Admixtures. $t=50$ degrees centigrade. (A) Electromotive force (in mV); (B) Amount of NaOH (in milligrams). Solution Compo-

sition: (1) 38 g/l Ni; (2) 38 g/l Ni+0.16 mol/l H_3BO_3 ; (3) 38 g/l Ni+0.16 mol/l NH_4Cl ; (5) 38 g/l $NiNO_3$ +0.16 mol/l NH_4NO_3 .

The effect of the concentration of ammonium sulphate on the value of pH at the initial moment of nickel hydrate formation is shown in Table 2.

The data of Table 2 is represented by curve 1 in Figure 4. in the same figure, for comparison, we show an analogous curve 2 for the values of pH at the initial moment of hydrate formation from solutions with admixtures of boric acid [1]. By comparing the two curves we see clearly that ammonium sulphate lowers the value of pH more sharply than boric acid. The data shown is significant if we want to clarify the formation mechanism of nickel precipitates with heightened hardness, in the presence of ammonium sulphate.

Since the hydrates begin to form at a lower value of pH in solutions with ammonium sulphate admixture than in solutions with boric acid, it is natural that there will be more hydrates and that the precipitates will be harder with the former conditions of electrolysis than with the latter.

FIGURE 3

Potentiometric Titration Curves of the Nickel Electrolyte with an Addition of $(NH_4)_2SO_4$ as a Buffer. $t=50$ degrees centigrade. (A) Electromotive Force (in mV); (B) Amount of NaOH (in milligrams). Electrolyte: Ni (in sulphate form) -- 38 g/l; NaCl -- 5 g/l; Na_2SO_4 -- 40 g/l; $(NH_4)_2SO_4$: (1) -- 10 g/l, (2) -- 20 g/l, (3) -- 40 g/l

The experimental data obtained allows us to draw certain conclusions about the composition of the solid phase.

In fact, if we assume that the formation of the solid phase begins when the solubility product of the type

$$a_{\text{Me}^n+} \cdot a_{\text{OH}^-}^n = L_p, \quad (1)$$

is reached, i.e. that, at least at the moment of its appearance, the solid phase constitutes a pure hydrate rather than the basic salt, then the values of the solubility products should not vary with the change of nickel sulphate concentration.

For a clearer formulation of this law we conducted supplementary experiments titrating diluted solutions of nickel sulphate. The results of these are shown in Figure 5. The practical computation of L_p on the basis of activity coefficients will hardly be sufficiently accurate, since the latter are known only up to a temperature of 25 degrees centigrade. True, a comparison of the activity coefficients at 25 degrees [3] and at a temperature close to the freezing point of the solutions [4], show that they vary but slightly with temperature. Table 3 shows the results of the computations of L_p according to all experimental data obtained.

Table 1

EFFECT OF BUFFER ADMIXTURES ON THE VALUE OF PH AT THE INITIAL MOMENT OF
NICKEL HYDRATE FORMATION AT 50 DEGREES CENTIGRADE IN SOLUTIONS CONTAIN-
ING 38 g/l OF Ni

| Name of Buffer Admixture (0.16 mol/l) | Value of pH at the Initial Moment of Nickel Hydrate Formation in Various Solutions | | |
|---|--|-------------------|-----------------------------------|
| | NiSO ₄ | NiCl ₂ | Ni(NO ₃) ₂ |
| | | | |
| Absent | 5.3 | 4.9 | 4.8 |
| H ₃ BO ₃ | 4.3 | 3.4 | 3.3 |
| (NH ₄) ₂ SO ₄ | 3.5 | 3.5 | 3.3 |
| NH ₄ Cl | --- | 3.3 | ? |
| NH ₄ NO ₃ | --- | --- | ? |

Table 2

EFFECT OF AMMONIUM SULPHATE CONCENTRATION ON THE VALUE OF pH AT THE
INITIAL MOMENT OF NICKEL HYDRATE FORMATION

Ni -- 38 g/l, NaCl -- 5 g/l

Na₂SO₄ -- 40 g/l. t=50 degrees centigrade

| Concentration (NH ₄) ₂ SO ₄ (in g/l) | Value of pH at Initial Moment of Hydrate Formation |
|---|---|
| 0 | 5.2 |
| 10 | 3.9 |
| 20 | 3.6 |
| 40 | 3.4 |

FIGURE 4

Effect of Ammonium Sulphate Concentration and of Boric Acid on the Value of pH at the Initial Moment of Nickel Hydrate Formation at 50 degrees centigrade (A) Value of pH at the Initial Moment of Hydrate Formation; (B) Concentration of buffer admixture (in mol/l). (1) -- with admixture of ammonium sulphate; (2) -- with admixture of boric acid.

FIGURE 5

Potentiometric Titration Curves of Diluted Nickel Sulphate Solutions with a Glass Electrode at 50 Degrees Centigrade. (A) Electromotive Force (in mV); (B) Amount of NaOH (in milligrams): Ni Content (in g/l): (1) -- 0.05; (2) -- 0.1; (3) -- 0.5; (4) -- 1.5; (5) -- 5.

As we see from the Table, the values of L_p do not remain constant, but decrease regularly 137 times as the nickel concentration is brought from 0.05 g/l to 61 g/l. Therefore, we also computed L_p , utilizing the values of the apparent dissociation degree of nickel sulphate.

See Table 3 on page 7

For this calculation we took the following essential values:
 $K_{w50^\circ} = 5.6 \cdot 10^{-14}$ (5); $\frac{11}{2} \text{ Ni}^{++} = 46$; $\Delta_{\text{Ni}} = 0.024$; $\frac{1}{2} \text{ l } 50^\circ$
 $\lambda_{\text{Ni}}(18^\circ) = 68$; $\Delta_{50^\circ} = 0.0227$; and therefore: $\lambda_{\infty 50^\circ} = 188$. The values of λ_{V50° are taken from the tables [6] (partially extrapolated).

Table 3

DATA OF THE SOLUBILITY PRODUCT COMPUTATION ACCORDING TO EXPERIMENTAL DATA

| [1] Nickel Concentration | | [2] pH at Start of Hydrate Formation | [3] Computation of L_p on the Basis of Activity Coefficients | | | [4] Computation of L_p on the Basis of Apparent Dissociation Degree | | | |
|--------------------------------|---------------------|--|--|---------------------|----------------------------|---|--|--------------------------|----------------------------|
| [a] in g/l | [b] in mole/l | | [c] f | [d] $\lg a_{Ni}$ | [e] $L_p \cdot 10^{16}$ | [f] λ_v 50° | [g] $\alpha = \frac{\lambda_v}{\lambda_\infty}$ | [h] $\lg C_{Ni^{++}}$ | [i] $L_p \cdot 10^{15}$ |
| 0.05 | 0.0009 | 7.1 | 0.80 | 4.857 | 3.58 | 158 | 0.84 | 4.903 | 3.46 |
| 0.10 | 0.0017 | 7.0 | 0.70 | 3.076 | 3.73 | 151 | 0.80 | 3.114 | 4.28 |
| 0.5 | 0.0085 | 6.7 | 0.48 | 3.613 | 2.03 | 111 | 0.58 | 3.778 | 3.14 |
| 1.5 | 0.0256 | 6.3 | 0.32 | 3.914 | 1.02 | 92 | 0.49 | 2.097 | 1.55 |
| 5.0 | 0.0884 | 6.1 | 0.18 | 2.20 | 0.76 | 71 | 0.38 | 2.524 | 1.60 |
| 10 | 0.170 | 5.8 | 0.14 | 2.377 | 0.30 | 64 | 0.34 | 2.762 | 0.72 |
| 21 | 0.362 | 5.6 | 0.094 | 2.532 | 0.11 | 55 | 0.29 | 1.025 | 0.33 |

| [1] | | [2] | [3] | | [e] | [4] | | | |
|------|-------|-----|-------|-------|-------|-----|------|-------|------|
| [a] | [b] | | [c] | [d] | | [f] | [g] | [h] | [i] |
| 25 | 0.430 | 5.5 | 0.084 | 2.558 | 0.07 | 53 | 0.28 | 1.100 | 0.24 |
| 35 | 0.605 | 5.3 | 0.068 | 2.613 | 0.05 | 51 | 0.27 | 1.215 | 0.20 |
| 36 | 0.614 | 5.3 | 0.066 | 2.608 | 0.05 | 51 | 0.27 | 1.215 | 0.20 |
| 39 | 0.665 | 5.3 | 0.063 | 2.621 | 0.05 | 50 | 0.27 | 1.248 | 0.22 |
| 39.6 | 0.675 | 5.3 | 0.062 | 2.621 | 0.05 | 50 | 0.27 | 1.248 | 0.22 |
| 40.6 | 0.693 | 5.3 | 0.061 | 2.625 | 0.05 | 49 | 0.26 | 1.255 | 0.22 |
| 51 | 0.869 | 5.2 | 0.054 | 2.671 | 0.04 | 48 | 0.26 | 1.364 | 0.17 |
| 61 | 0.040 | 5.1 | 0.051 | 2.724 | 0.026 | 46 | 0.24 | 1.406 | 0.12 |

With this method of computation, the solubility product also does not remain constant (the change is 29-fold).

If we plot on a graph the values of pH at the initial moment of hydrate formation as compared to the ion activity logarithm, then in correspondence with the developed equation (1)

$$\text{pH} = -\frac{1}{2} \lg a_{\text{Ni}^{++}} + \frac{1}{2} \lg L_p - \lg K_w \quad (2)$$

We must obtain a straight line with an angular coefficient

$$-\frac{d \text{pH}}{d \lg a_{\text{Ni}^{++}}} = \frac{1}{2} \quad (3)$$

FIGURE 6

Verification of Equation (2) According to the Data of Nickel Hydrate Formation. (A) Value of pH at the beginning of hydrate formation; (B) Activity logarithm (of concentration). (1) -- pH $\lg a_{\text{Ni}^{++}}$; (2) -- pH- $\lg C_{\text{Ni}^{++}}$.

Figure 6 shows the relation of the pH value at the beginning of hydrate formation to the activity logarithm or to the concentration of nickel ions. The value of the angular coefficient required by theory is obtained only in the border line case of the titration of very diluted solutions. Upon titration of concentrated solutions the value of the angular coefficient turns out to be higher than in theory.

A different correlation takes place in the case of hydrate formation by admixtures in a nickel solution. Applying the known rule that an electrolyte, in the presence of a large and constant

excess of another electrolyte, behaves as an ideal substance, we may transcribe equation (2) for pH at the initial moment of admixture hydrate formation, thus:

$$\text{pH} = -\frac{1}{2} \lg a_{\text{Ni}^{++}} + \frac{1}{2} \lg L_p - \lg K_w \quad (4)$$

where m is the valency of the cations. Then in the co-ordinates of $\text{pH} - \lg C_{\text{adm}}$, we must obtain straight lines with the conventional coefficient $\frac{1}{2}$ for ferrous and cuprous salts and $\frac{1}{3}$ for ferric salts. As may be seen in Figure 7, this condition of theory is fulfilled.

FIGURE 7

Verification of Equation (4) According to the Data of Formation of Hydrates of Copper and of Bi and Tri-Valent Iron in a Nickel Electrolyte. (A) Value of pH at the initial moment of Hydrate formation (for bi-valent metals); (B) Same for tri-valent metals. (1) -- Fe^{+++} with H_3BO_3 admixture; (2) -- Fe^{+++} without H_3BO_3 ; (3) -- Fe^{++} ; (4) -- Cu^{++} .

Thus it follows from the data obtained that upon titration of very diluted nickel sulphate solutions and also of admixtures in a nickel electrolyte, the composition of the solid phase formed, corresponds to the formula of the corresponding hydrate. It must be noted that a similar conclusion was reached through experiments on the titration of alkaline cadmium sulphate solutions with simultaneous measurement of pH by a glass electrode, of the concentration of cadmium ions by a cadmium electrode, and of the sulphate ions by a lead electrode [7].

Upon titration of more concentrated nickel sulphate solutions, the composition of the solid phase obtained, becomes more complicated because poorly soluble nickel basic salts, rather than the pure hydrates are formed.

Under conditions of common hydrolysis, there occurs in the electrolyte layer next to the cathode, a sharp impoverishment of nickel by the ions and an increase in alkalinity on the entire surface of the electrolyte. This creates conditions favorable to the formation of hydrates, rather than of insoluble basic nickel salts. Consequently, if we assume that the minute crystallinity of the nickel precipitates is caused by the formation either of colloid hydrates or of basic salts in the process of electrolysis, then the experimental material available forces us to give preference to the hypothesis of the formation of hydrates instead of the formation of basic compounds.

CONCLUSIONS

(1) With the method of potentiometric titration with a glass electrode, and also with the help of ^{Tyndall} Tyndal's cone, we determined the values of pH at the initial moment of nickel hydrate formation in sulphate, chloride and nitrate solutions.

We showed that the value of pH at the initial moment of hydrate formation in chloride and nitrate solutions is the same, while in a sulphate solution the precipitation of hydrates begins in a more alkaline medium.

(2) Admixture of boric acid lowers the value of pH at the beginning of nickel hydrate formation more sharply in chloride and

nitrate solutions than in sulphate solutions.

(3) We studied the effect of ammonium sulphate on the lowering of the value of pH at the initial moment of hydrate formation, and we showed that in a sulphate solution its effect is stronger than that of boric acid, while in the chloride and nitrate solutions the effect of both buffer admixtures is approximately the same.

(4) The increased hardness of the cathode precipitates obtained from solutions with ammonium sulphate admixture and under average electrolysis conditions, is conditioned, apparently, by the large amount of nickel hydrates in the layer next to the cathode.

(5) On the basis of an analysis of experimental data we showed that under nickel electrolysis conditions it is more likely that colloid hydrates of metals rather than their basic compounds are generated.

LITERATURE

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Reached the Editors

January 20, 1950

Note for the Reader. Thanks to a defect in the calibrated chart of the glass electrode, our preceding works were incorrect in computing the electromotive forces in the relation to the values of pH. The correct values of pH at the initial moment of hydrate formation are given at the end of this issue on page 680.

Corrected Tables Belonging to the Articles by A. L. Rotinyan
and V. Ya. Zel'des

Report I (Zhurnal Prikladnoy Khimii 23, 717, 1950)

Table 1

| Con of Ni (g/l) | pH |
|--------------------|-----|
| 10.0 | 5.8 |
| 25.0 | 5.4 |
| 39.6 | 5.3 |
| 61.0 | 5.1 |

Table 4

| Con of H ₃ BO ₃ (g/l) | pH at NaCl 5 | con 50 |
|--|--------------------|-----------|
| 0 | 5.3 | 5.2 |
| 10 | 4.7 | 4.3 |
| 20 | 4.3 | 4.0 |
| 40 | 3.7 | 3.4 |

Table 5

Table 5

| Temp (°C) | pH at con of Ni (g/l) | | |
|--------------|--------------------------|-----|-----|
| | 21 | 40 | 63 |
| 20 | 5.2 | 5.0 | 4.8 |
| 50 | 4.4 | 4.3 | 4.1 |
| 70 | 3.8 | 3.7 | 3.6 |

The value of the pH quantity at the moment of beginning hydrate formation decreases by approximately 0.26 unit with increase of temperature each 10°C.

In Tables 2 and 3 all derived values of pH should be decreased by 0.4.

Report II (Zhurnal Prikladnoy Khimii 23, 936, 1950)

Table 1

| Con of Ni (g/l) | pH | |
|--------------------|---|--|
| | H ₃ BO ₃ 0 g/l | H ₃ BO ₃ 20 g/l |
| 0.004 | 5.3 | - |
| 0.05 | 5.1 | - |
| 0.19 | 5.0 | 4.2 |
| 0.50 | 4.7 | - |
| 0.98 | 4.5 | 4.0 |
| 3.11 | 4.3 | 3.9 |

Table 3

| Con of ferrous oxide (g/l) | | pH |
|-------------------------------|-------|-----|
| before | after | |
| 0.00 | 0.00 | 5.3 |
| 0.09 | 0.06 | 5.0 |
| 0.49 | 0.43 | 4.7 |
| 1.08 | 1.00 | 4.4 |
| 3.90 | 1.85 | 4.3 |

These correction do not reflect in any way upon the text material and conclusions of the indicated works.

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END OF CORRECTIONS